anionic chelating and bridging ligand xanthopterinate (=xanth).

$$(A)_2MoO_4{\cdot}2H_2O + {}^1/_7(NH_4)_6Mo_7O_{24}{\cdot}4H_2O +$$

A = Na, TEA

$$2\ \text{xanthopterin} \xrightarrow[80\ {}^\circ\text{C},\ <1\ \text{h}]{Me_2SO} (A)_2Mo_2O_5(\text{xanth})_2$$

Use of ammonium heptamolybdate in the reaction is critical to formation of the product in high yields. The dinuclear complex is moisture sensitive and degrades in the atmosphere or in wet solvents to xanthopterin and an unidentified polymolybdate. The dimeric complex does not react with triphenyl phosphine when heated at 110 °C for 4 h. However, treatment with the protic reactants dithiothreitol ($dttH_2$) or 3,4-toluenedithiol ($tdtH_2$) precipitates xanthopterin with formation of a molybdenum–oxo–dtt complex or $Mo(tdt)_3$, respectively, as identified by TLC.

The electronic spectrum of xanthopterin in DMF shows an absorption at 390 nm (ϵ = 3360 cm^{-1} M^{-1}) that shifts to 424 nm (ϵ = 2400 cm^{-1} M^{-1}) upon deprotonation to the dianionic form in strong base.[8] The corresponding λ_{max} for the Na^+ and TEA^+ salts of $Mo_2O_5(xanth)_2^{2-}$ in DMF are 418 nm (ϵ = 6820 cm^{-1} M^{-1}) and 424 nm (ϵ = 6910 cm^{-1} M^{-1}), respectively, suggesting that xanthopterin exists in a doubly deprotonated form in the molybdenum complex. Infrared data[9] from both salts of the dimer suggest coordination through both oxygen atoms of the pterin since the strong $\nu_{C=O}$ absorptions of xanthopterin at 1680 and 1660 cm^{-1} are absent in the product spectrum. Absorptions typical[10] of terminal Mo═O and bridging Mo–O–Mo groups of the $[Mo_2O_5{}^{2+}]$ unit were observed near 930, 900 cm^{-1} and 785, 765 cm^{-1}, respectively.

The crystal structure[13] of $[Na(Me_2SO)_2]_2Mo_2O_5(xanth)_2$ confirms the chelation mode of the xanthopterin ligand. One view of the oxo–molybdenum dianion is shown in Figure 1. Selected bond distances and angles are given in Table I.

The dimolybdenum dianion consists of a *syn*-$[Mo_2O_5{}^{2+}]$ unit chelated and bridged by two xanthopterinate ligands. A noncrystallographic molecular 2-fold symmetry axis passes through the bridging oxygen in a plane perpendicular to the Mo–Mo axis. In $[Mo_2O_5(xanth)_2]^{2-}$ coordination of the two oxygen atoms of each pterin ligand to different Mo atoms favors formation of the less common *syn*-$[Mo_2O_5]^{2+}$ unit.[11] Each molybdenum is bound to O3 and N5 of one xanthopterin forming a five-membered chelate ring analogous to that of 8-hydroxyquinolinate. This binding mode is analogous to the "primary binding site"[4f] observed in flavins coordinated to Ru(II),[4e] Cu(I), Cu(II),[4f] and Ag(I).[4g] The second oxygen atom, O4, bridges the xanthopterin ligand to the second molybdenum. The inner coordination sphere about each Mo is a distorted octahedron (see Table I) of one nitrogen and five oxygen atoms. The two terminal Mo–oxygen bond lengths on each Mo atom are slightly different, likely due to the interaction of the sodium counterions with O_{a2} and O_{b1}.

The pterin rings are planar and this planarity extends through the Mo bound to atoms O3 and N5. The dihedral angle between pterin planes is 47.3°, a value very close to the angle observed in a related catecholate complex, $[Mo_2O_5(3,5\text{-dibutylcatecholate})_2]$.[11a] The sodium cations establish a three-dimensional crystal lattice by connecting the dianions. Each of the counterions is bound to one terminal oxo ligand and one xanthopterin oxygen and connects to adjacent dianions through pterin nitrogens N1 and N8. The remaining coordination sites of each six-coordinate sodium atom are filled by oxygen atoms of two dimethyl sulfoxide solvent molecules.

Coordination of xanthopterin by molybdenum has a large effect on the ligand's fluorescence properties. Chelation quenches the fluorescence intensity by 95% compared to that of free xanthopterin. The close resemblance of the spectra from solutions of the Mo dimers to that of xanthopterin suggests that the observed fluorescence is due to dissociated, neutral ligand (formed by trace acid hydrolysis). Previously, the disappearance of fluorescent character in pterins has been attributed to their reduction of di- and tetrahydro forms.[12] Clearly, metal coordination also leads to fluorescence quenching.

The results of these initial studies on molybdenum–pterin coordination chemistry show (a) structural proof for molybdenum coordination through endocyclic nitrogen atoms and exocyclic oxygen atoms in pterin heterocycles and (b) effective quenching of a highly fluorescent pterin by coordination to molybdenum.

Registry No. $Na_2Mo_2O_5(xanth)_2$, 105139-37-5; $[TEA]_2Mo_2O_5(xanth)_2$, 105226-34-4; $Mo(tdt)_3$, 10507-75-2; dtt, 3483-12-3; Mo, 7439-98-7; $[Na/(Me_2SO)_2]_2Mo_2O_5(xanth)_2$, 105227-46-1; xanthopterin, 119-44-8; MO, 7439-98-7.

Supplementary Material Available: Tables of atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms (6 pages); structure factor tables for $[[Mo(O)_2(O_2N_5C_6H_3)]_2O]\text{-}Na_2{\cdot}4(CH_3)_2SO$ (18 pages). Ordering information is given on any current masthead page.

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[8] $TEA_2(xanth)$ was prepared by dissolving xanthopterin in methanol by dropwise addition of 2 equiv of TEAOH (as a 25% methanolic solution) then precipitating the salt with diethyl ether.

[9] Infrared data (KBr, cm^{-1}): $[Na{\cdot}(dmf)_2]_2Mo_2O_5(xanth)_2$ ν_{NH} 3395 s, 3340 s; $\nu_{C=O}$(dmf) 1663 vs; $\nu_{C-O,C-N}$ 1616 m, 1565 s, 1538 vs; $\nu_{Mo=O}$ 934 s, 906 sh, 902 s; $\nu_{Mo-O-Mo}$ 782 ms, 768 m; ν_{Mo-O},ν_{Mo-N}(ligand) 683 w, 665 m, 630 m, 560 m. $TEA_2Mo_2O_5(xanth)_2$ ν_{NH} 3415 s, 3305 m; $\nu_{C=O,C=N}$ 1620 m, 1554 vs, 1538 s; $\nu_{Mo=O}$ 926 s, 904 s, 899 s, 894 sh; $\nu_{Mo-O-Mo}$ 785 ms, 760 s; ν_{Mo-O},ν_{Mo-N}(ligand) 684 w, 629 m, 616 m, 552 m.

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[13] Crystals of $[Na(Me_2SO)_2]_2[Mo_2O_5(xanth)_2]$ were grown from Me_2SO/THF. A yellow-orange rectangular parallelepiped of approximate dimensions 0.45 × 0.45 × 0.52 mm was glued to the inside of a thin-walled capillary and sealed with mother liquor. Data were collected on a Nicolet four-circle autodiffractometer using Mo Kα radiation and the structure was solved by Dr. Cynthia Day of Crystalytics Co. The compound crystallizes in the triclinic lattice system, space group $P1$, having cell dimensions a = 9.404 (2) Å, b = 9.412 (2) Å, c = 23.721 (5) Å and α = 92.18 (2)°, β = 92.01 (2)°, γ = 90.22 (2)° giving V = 2097 (1) $Å^3$ and a calculated density of 1.560 g/cm^3 for Z = 2. The structure was solved by using direct methods. Hydrogen atoms on amino nitrogens N_a and N_b were located from a difference Fourier synthesis and refined as isotropic spheres. All other hydrogen positions were calculated assuming C–H distances of 0.96. Final least-squares refinement on 551 parameters used 4085 unique data having $I > 3\sigma(I)$ and gave residuals R = 4.8 and R_w = 5.6% and GOF of 2.63.

Phenyl-Capped Octaaniline (COA): An Excellent Model for Polyaniline

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Received September 11, 1986

In this paper we report that the title compound can be characterized in three stable oxidation states: the reduced, COA (leuco, B_7),[1] the fully oxidized (tetraquinone imine, "TQI", B_3Q_4, old nomenclature "pernigraniline"), and the intermediate oxidation state, B_5Q_2 ("emeraldine"). The properties of these materials, particularly as a function of pH, showed that B_5Q_2 is an excellent model of polyaniline (PANI) because it exhibits all the properties of the polymer, particularly Brönsted acid doping.[2]

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[1] Besides the two capping phenyl groups, in COA there are seven *p*-phenylene rings (benzenoid group, B) in the backbone. Oxidation of one of the backbone B's produces a quinone imine (quinonoid group, Q); the resulting backbone would then be B_6Q. Thus this nomenclature: B_7 (COA), B_6Q (COA-BI), B_5Q_2 (COA "emeraldine"), B_4Q_3 (COA-"nigraniline"), and B_3Q_4 [COA pernigraniline or tetraquinone imine (TQI)].

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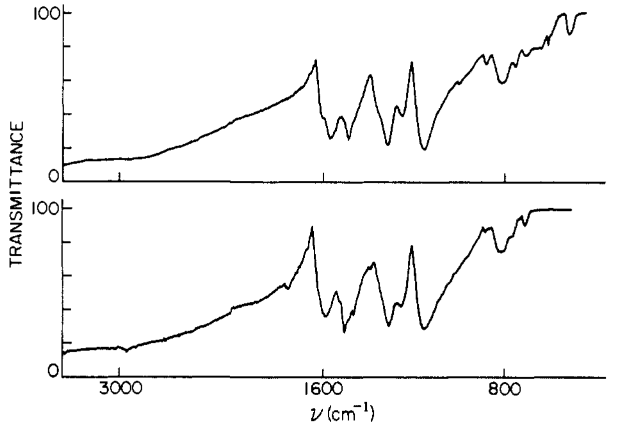
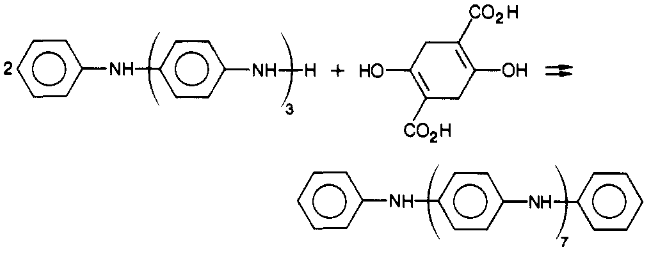


Figure 1. Infrared spectra (KBr) of $B_5Q_2{\cdot}4HCl{\cdot}3H_2O$ (top) and PANI·HCl (bottom).

Scheme I



COA

The crude product, prepared[3] according to Scheme I,[2a] consisted of mostly B_6Q as determined from its color and electronic spectrum (weak absorption at 620 nm, see Figure 3). Reduction of B_6Q with phenylhydrazine and recrystallization from DMF containing a trace of phenylhydrazine afforded clumps of white microcrystals of B_7[3] which slowly turned blue when exposed to the atmosphere.

Two equivalents of ammonium persulfate in aqueous 1.0 M HCl (conditions which produce PANI from aniline) converted B_7 to deep green HCl salt of B_5Q_2[4] whose four-probe compressed pellet conductivity was ~ 1 S cm^{-1} (same order of magnitude as PANI!)[2] and whose ESR ($g = 2.0036$, 0.6 spins/molecule), IR (cf. Figures 1 and 2), and UV-vis spectra (Figure 3) were identical with that of Brönsted acid doped polyaniline.[2] Dilute aqueous ammonia converted the green solid to a blue-black insulator (same behavior as PANI, conductivity of $<10^{-7}$ S cm^{-1}) whose spectral features corresponded to those of PANI; phenylhydrazine converted it back to B_7, indicating that ammonium persulfate did not effect the polymerization of B_7 to PANI.

Excess lead dioxide in DMF, at room temperature, converted B_7 to B_3Q_4,[5] a dark violet ("pernigraniline") solid, soluble in chloroform and slightly soluble in hot benzene.

In summary, we have demonstrated that (1) a monodisperse polyaniline of MW 806 can be prepared; (2) it can be converted to a partially oxidized form, B_5Q_2, which exhibits the same spectroscopic properties and *same conductivity* as that of the product from ammonium persulfate oxidation of aniline; and (3) it can be completely oxidized to a polyimine. The significance of these results is that the high conductivity of such a low molecular weight oligomer demands that the charge carriers are localized on a few aniline units and that an *intermolecular* mechanism for charge transport is predominant in Brönsted acid "doped" B_5Q_2 and, by inference, in PANI. From these results we conclude that qualitatively *PANI can be represented fully by COA*[6] and that Wilstätter[7] and Wnek's[8] hypotheses are sub-

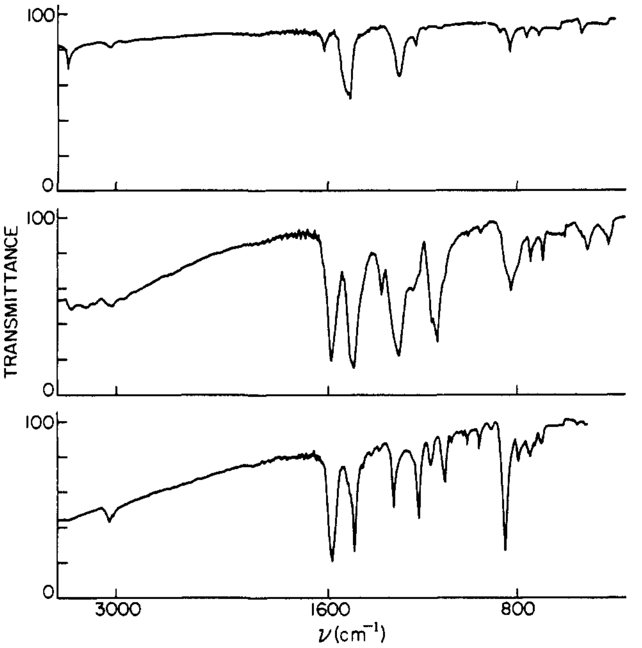


Figure 2. Infrared spectra (KBr) of COA (top), B_5Q_2 (middle), and B_3Q_4 (bottom), note that the C=N stretching assignable to B_5Q_2 (1598 cm^{-1}) and B_3Q_4 occurs at exactly the same frequency as the aromatic C=C stretching vibration in pristine, white COA.

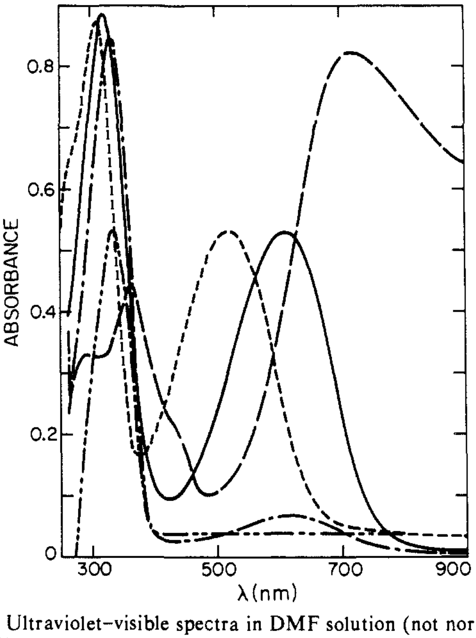


Figure 3. Ultraviolet-visible spectra in DMF solution (not normalized) of four different oxidation states of COA and of $B_5Q_2{\cdot}4HCl{\cdot}3H_2O$. COA (-··); ($B_6Q$) (-·); B_5Q_2 (—); B_3Q_4 (- - -); $B_5Q_2{\cdot}4HCl{\cdot}3H_2O$(-).

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(3) Two equivalents of tetraaniline[7] and 1 equiv of dihydroxydihydroterephthalic acid (obtained through reduction of dihydroxyterephthalic acid, (cf.: Baeyer, A.; Noyes, W. *Chem. Ber.* **1889**, *22*, 2168) were allowed to condense in distilled, degassed *m*-cresol over 48 h under an inert atmosphere, followed by overnight exposure to air. Dilution with ether, followed by filtration, afforded B_6Q in 60% yield., UV-vis (DMF) λ_{max} 332 ($\epsilon = 8.84 \times 10^4$), 618 nm ($\epsilon = 6.97 \times 10^3$). Stirring with excess phenylhydrazine in DMF, followed by copious washing with benzene, afforded B_7. Anal. calcd for $C_{54}H_{46}H_8$: C, 80.40; H, 5.71; N, 13.90. Found: C, 80.53; H, 5.66; N, 13.69. UV-vis (DMF) λ_{max} 334 nm ($\epsilon = 7.44 \times 10^4$). Ir, see Figure 2. Mp (DSC) 330 °C, followed by decomposition at 358 °C.

(4) Anal. calcd for $C_{54}H_{46}Cl_4N_8{\cdot}3H_2O$: C, 64.67; H, 4.9; Cl, 4.17; N, 11.18; O, 4.79. Found: C, 65.36; H, 4.97; Cl, 14.01; N, 11.26 (by difference), O, 4.40. UV-vis (see Figure 3), IR (see Figure 1).

(5) MS 798; IR (KBr, cm^{-1}) 3045 w, 1580 s, 1490 s, 1320 m, 1215 m, 1165 w, 1105 m, 1085 w 1025 w, 1010 w, 955 w, 910 w, 850 s, 795 w, 745 w, 700 w; UV-vis (DMF) λ_{max} 320 ($\epsilon = 4.35 \times 10^4$), 525 nm ($\epsilon = 2.57 \times 10^3$).

(6) The most recent attempt to model PANI with a small oligomer dealt with independent measurements on *N,N'*-diphenyl-*p*-phenylenediamine and *N,N'*-diphenylbenzoquinone imine: McManus, P. M.; Yang, S. C.; Cushman, R. J. *J. Chem. Soc., Chem. Commun.* **1985**, 156. A tetraaniline model was recently studied by: Cao, Y.; Li, S.; Zhijiann, X.; Guo, D. Preprint, 1986. Wolfe, J. *Abstracts of Papers*, 192nd National Meeting of the American Chemical Society, Anaheim, CA; American Chemical Society: Washington, DC, 1986.

stantially correct.

Acknowledgment. We are indebted to Office of Naval Research for support of this work. We thank Hugh Webb for mass spectroscopy, R. O. Angus for fundamental research on reactions of dihydroxydihydroterephthalic acid, and Z. X. Liu for four-probe conductivity measurements.

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Direct Formation of a Tricyclic Cycloheptanone-Containing System by Enolate Condensation with a Cyclopropanone Derivative

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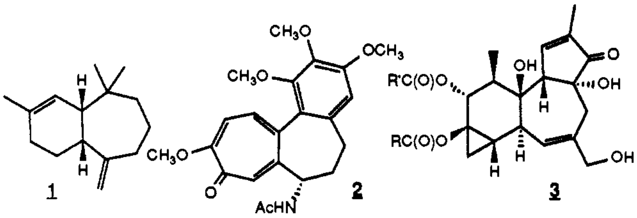
Received August 18, 1986

Seven-membered carbocycles occur among many classes of natural products. Most commonly, the seven-membered ring is bound to at least one additional ring of another size. Especially well-known examples are the guaianes and pseudoguaianes,[1] but other cases include the himachalenes (e.g., α-himachalene, **1**),[2] colchicine (**2**),[3] and the phorbol esters (e.g., **3**).[4] Because of the importance of these compounds, many methods have been devised for the construction of cycloheptane derivatives.[5] However, we now report the very direct formation of a tricyclic cycloheptanone-containing system in a one-pot reaction sequence, which is based upon the condensation of an enolate with a cyclopropanone derivative and which apparently employs the homoenolate reactivity of a cyclopropanoxide intermediate.[6]



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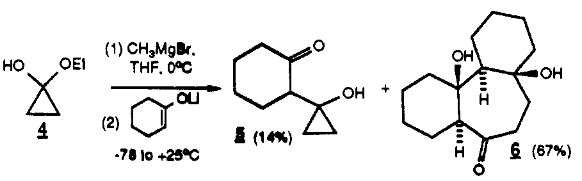
Reaction of the readily available cyclopropanone ethyl hemiacetal (**4**)[7] with methylmagnesium bromide followed by the addition of lithium cyclohexenolate affords a mixture of products composed of the formal cyclopropanone adduct **5** in 14% yield and, much more interestingly, the tricyclic product **6** in 67% yield (eq 1). A small amount (3%) of starting material **4** is recovered,



(1)

but other components, present in trace quantities in the reaction mixture, have not been identified.

Determination of the structure of product **6** was initially difficult, even with the use of 300-MHz ^{1}H NMR and europium shift reagent studies. However, the ^{1}H NMR spectrum obtained at 600 MHz is sufficiently resolved to permit assignment of the indicated structure.[8] Subsequent single-crystal X-ray diffraction studies (Figure 1) confirm this assignment.[9]

In order to probe the pathway by which **6** is formed, we have done a number of further experiments, the most important of which are summarized here. When the simple adduct **5** is isolated from the original reaction mixture, purified, and then subjected to further reaction with methylmagnesium bromide and lithium cyclohexenolate, tricyclic **6** is obtained in 80% yield (eq 2). Silylation of adduct **5** to give **7** followed by reaction with lithium cyclohexenolate permits isolation of the further adducts **8–10** (eq

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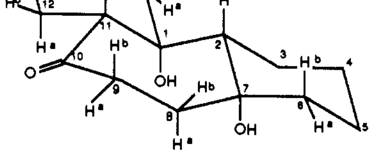
[8] The 600-MHz ^{1}H NMR spectrum of **6** ($CDCl_3$; after exchange with



6

D_2O) was obtained at Carnegie-Mellon University: δ 2.92 (dd, J = 12.7, 4.3 Hz, H_{11}), 2.75 (ddd, J = 15.8, 12.3, 6.0 Hz, H_{9b}), 2.41 (ddd, J = 15.9, 5.9, 2.6 Hz, H_{9a}), 2.25 (br d, J = 13.4 Hz, H_{12a}), 2.14 (ddd, J = 15.2, 12.4, 6.0 Hz, H_{8a}), 2.02 (dq, J = 13.9, 3.7 Hz, H_{12b}), 1.89 (br d, J = 13.4 Hz, H_{6b}) 1.83 (ddd, J = 14.9, 6.0, 2.6 Hz, H_{8b}), 1.80 (br d, J = 13.4 Hz, H_{6a}), 1.74 (br d, J = 13.0 Hz, H_{15b}), 1.45–1.64 (m, 8H, CH_2), 1.35 (dd, J = 12.2, 3.4 Hz, H_2), 1.07–1.24 (m, 3 H, CH_2).

[9] Compound **6** crystallized in the monoclinic space group $P2_1$ with a = 5.808 (2) Å, b = 9.036 (4) Å, c = 12.839 (3) Å, and β = 97.68 (2)°. The structure was solved with Multan (189 reflections with a minimum E of 1.54 and 1404 relationships), using 1518 unique reflections with $F_o^2 > 2.0\sigma(F_o^2)$ ($2\theta \leq 48.3°$) measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. Refinement with anisotropic temperature factors and calculated hydrogen atom positions led to R = 0.038 and R_w = 0.059. Complete details of this structure determination will be reported in our full paper on the cycloheptanone annulation.

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